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University of Kinshasa, Democratic
Republic of Congo
Anupam Banerjee,

Indian Institute of Technology Kanpur, India

*CORRESPONDENCE

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Genesis of the Bayan Obo Fe-REE deposit: evidence from Mg isotope and geochemistry of siderite carbonatites, Inner Mongolia, China

Chenghao Ren¹, Hongxiang Jia¹*, Qunmao Zhou², Hongquan She¹, Jinwen Li¹ and Baoliang Li¹

¹Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, China, ²Research Institute of Exploration and Development, PetroChina Xinjiang Oilfield Company, Karamay, Xinjiang, China

The Bayan Obo Fe-REE deposit, a world-renowned giant polymetallic ore concentration area, is located on the northern edge of the North China Craton, which borders on the Central Asian orogenic belt. Many studies have been conducted since the primary orebody was discovered, but its genesis has always been a fiercely debated issue. In recent years, the rapid development of Mg isotope research has shown promise in tracing mantlederived igneous rocks and carbonatites, providing a new approach to studying the formation of the Bayan Obo deposit. In this study, we conducted Mg isotope composition and whole-rock geochemical analysis on the siderite carbonatites closely associated with the formation of the Bayan Obo deposit to reveal its genesis. Results show that the siderite carbonatites have high levels of Sr (796.3-6,343.1 ppm), Ba (84.8-11593.0 ppm), and Mn (8,319.8-48680.8 ppm), as well as rare earth element abundance (2,696.8-20763.6 ppm), distinguishing them from sedimentary carbonate rocks. The $\delta^{26} Mg$ variation range for the siderite carbonatites is -1.31 to -0.09%, with a mean value of -0.37%, similar to characteristics of dolomite carbonatites in the mining area. Integrating the results of this study with previous research, we propose that the Bayan Obo deposit formed through the intrusion of carbonatitic magma and subsequent metasomatic processes. The genesis of the deposit was primarily governed by mantle-derived carbonatitic magmatism, with progressive magma differentiation and evolution likely facilitating the enrichment of Fe, REE, Sr, Ba, and Y.

KEYWORDS

siderite carbonatite, Mg isotope, whole-rock geochemistry, igneous carbonatite, genesis of ore deposit, Bayan Obo

1 Introduction

Bayan Obo is the world's largest rare earth element (REE) deposit, with a cumulative exploration of 1,160 Mt of iron ore, and 112 Mt of rare earth oxides (Chao et al., 1997; Xie et al., 2019). Its REE resources account for more than two-thirds of all known rare earth resources in the world. Except for iron and REE, the deposit is also

rich in critical minerals such as niobium (one of the world's largest niobium deposits), scandium, thorium, and fluorine. As a result, Bayan Obo has a significant economic and strategic position, drawing the interest of many geologists throughout the world.

The deposit was discovered in 1927 and has since undergone systematic geological investigations and, in places, mining development. Significant progress has been achieved in understanding its genesis, mineralization age, rare earth mineralogy, and other aspects, providing important contributions to REE mineralization theory (Zhang and Tao, 1996; Zhang P. S. et al., 1998; Zhang P. S. et al., 2001; Yang and Le Bas, 2004; She et al., 2023). The formation of the Bayan Obo deposit has undergone significant structural deformation and pervasive hydrothermal alteration, leading to complex geological and geochemical features. Numerous studies have been conducted on its metallogenic age, hydrodynamic history, mineralization processes, and genetic models (Smith et al., 2015; Fei et al., 2019). Previous studies have attributed the ore fluids of the Bayan Obo deposit to be source from sedimentary (Meng, 1982; Wei and Shangguan, 1983), sedimentary transformation metasomatism (Lai, 2013; Zhang Y. X. et al., 1998; Zhang et al., 2008; Hou, 1989; Qiao et al., 1997), submarine volcanic exhalation sedimentation (Yuan et al., 1991; Yuan et al., 1995; Bai and Yuan, 1985; Bai et al., 1996), volcanic institutions (Hao et al., 2002; Xiao et al., 2006; Xiao et al., 2012), subduction fluid metasomatism (Ling et al., 2013; Ling et al., 2014), high-temperature hydrothermal and mantle fluid metasomatism (Cao et al., 1994), carbonate rock magma hydrothermal fluids (Zhou et al., 1980; Liu, 1986; Wang et al., 2002), and carbonatite aegirinization (Wang et al., 2010; Wang et al., 2018; Elliott et al., 2018; Liu et al., 2018; Yang et al., 2019). In the last two decades, the relationship between mineralization and carbonatites has received increasing attention, particularly in the Bayan Obo deposit. Earlier studies generally regarded the ore-bearing dolomite as a sedimentary dolostone, but subsequent work has reinterpreted it as an igneous dolomitic carbonatite (Yang et al., 2009; Hu et al., 2023; Li et al., 2024). In parallel, two contrasting models have been proposed to explain the evolution of ore-forming fluids: (1) one links the genesis of REE mineralization to diagenetic processes associated with the emplacement of sedimentary dolostone, whereas (2) the other attributes the mineralization to igneous carbonatite intrusions in the region. Consequently, the origin and evolution of ore-forming fluids at Bayan Obo remain debated and continue to be a key issue in understanding the deposit's formation.

In the last two decades, increasing attention has been paid to the genetic relationship between mineralization and carbonatites, particularly regarding the reinterpretation of the Bayan Obo orebearing dolomite. Early studies generally considered this rock to be a sedimentary dolostone. However, subsequent research based on petrography, geochemistry, and isotopic evidence has demonstrated that it is better classified as an igneous dolomitic carbonatite related to carbonatite magmatism (Yang et al., 2009; Hu et al., 2023; Li et al., 2024). Nevertheless, debate persists regarding the diagenetic features of these ore-bearing dolomite carbonatites, which remains a key issue constraining the understanding of the formation and evolution of the Bayan Obo deposit.

Magnesium is one of the major elements in igneous carbonatites. As high-precision testing technologies for Mg stable isotopes rapidly advance (Galy et al., 2001; Galy et al., 2002; Chang et al.,

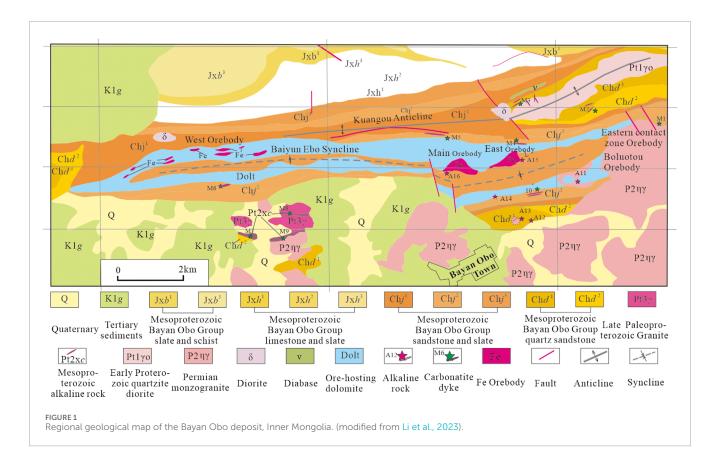
2003), Mg isotope geochemistry has become widely used in geological processes, such as recreating ancient marine habitats (Gothmanna et al., 2017; Riechelmann et al., 2016), tracking material cycles (Yang et al., 2012; Wang et al., 2016), and tracing the formation of mineral deposits (Ling et al., 2013; Tang et al., 2018). The advances and applications of Mg isotopes have been reviewed (He et al., 2008; Ge and Jiang, 2008; Teng, 2017). For example, Ke et al. (2011) were the first to summarize the Mg isotope composition of various material reservoirs on Earth and planets, and summarized the fractionation mechanism of Mg isotopes under high and low temperature conditions; Chen et al. (2021) mainly summarized the fractionation behavior of Mg isotopes in different geological processes and their application in carbonate rock research, and summarized the possible genesis mechanism of low δ^{26} Mg values in mantle derived rocks; Liu et al. (2023) systematically reviewed the application of Mg isotopes in the genesis of mineral deposits, porphyry genesis, geological thermometers, and fractionation mechanisms in endogenous geological processes. Therefore, Mg isotopic composition provides valuable information about the mineralization process and may be utilized to trace the origin of mineral deposits.

Despite that the Bayan Obo mining region is well known for siderite carbonatites associated with Fe, REE, and Nb mineralization, detailed investigations of these rocks are limited, and Mg isotopes have not previously been employed to elucidate their sources or evolutionary history. In this study, we present the first integrated investigation of Mg isotopes together with major-, trace-, and rare earth element geochemistry of siderite carbonatites, supported by field and petrographic observations. These results provide new insights into the petrogenesis of siderite carbonatites and offer important constraints on the genetic mechanisms of the Bayan Obo deposit.

2 Geological background

The Bayan Obo Fe-REE deposit is situated around 150 km north of Baotou City in Inner Mongolia, on the northern border of the North China Craton, adjacent to the Central Asian orogenic belt. The region has undergone complex tectonic evolution since the Proterozoic era (Zhao et al., 1999; Zhao et al., 2005; Zhai et al., 2015), including multiple rift events from the late Paleoproterozoic to the Neoproterozoic (Zhai et al., 2015), multistage magmatic processes related to subduction in the Paleozoic era (Zhang et al., 1994; Ling et al., 2014; Gao, 2022), and metamorphosis and deformation processes (Zhang et al., 2003; Smith et al., 2015). The long-term tectonic evolution has resulted in complex geological and geochemical characteristics mineral deposits and has also led to widespread controversy over the understanding of the mineralization background, mineralization era, and mineralization process of mineral deposits.

The Bayan Obo deposit is developed in the Middle Proterozoic Bayan Obo Group, which is divided into nine lithological sections (H1-H9), from bottom to top, H1-H7 is mainly quartz sandstone, feldspathic quartz sandstone, quartzite, with marl in the upper



part of the layer, H8 is mainly dolomite, H9 is mainly potassiumrich slate. The orebodies are mainly hosted in the dolomite of the H8 lithological section, forming an east-west ore belt with a length of about 18 km and a width of about 2-3 km. Within a range of 48 km², there are three mining areas from east to west (Figure 1). The two largest known as the Main Orebody and the East Orebody, are strongly affected by sodium and fluorine alteration, and rare earth, niobium, and iron mineralization are also very strong. In comparison, the western half of the ore-bearing zone, also known as the West Orebody, exhibits relatively weaker hydrothermal alteration and mineralization. Large areas of granite basement are exposed approximately 0.5-1 km east and south of the ore-bearing zone. The REE mineralization mainly occur in dolomite and it is hosted in fluorocarbonate series minerals and monazite (Zhang and Tao, 1996). Hundreds of carbonate dikes are distributed around the periphery of the mining region, intruding into the metamorphosed sedimentary rocks and basal gneiss layers of the Bayan Obo Group. According to the primary mineral composition, they are classified as dolomitic, calcitic, and dolomite-calcite coexisting carbonate dikes. Many scholars believe that the carbonate magmatism represented by carbonate dikes is intimately connected to Fe and REE mineralization (e.g., Liu et al., 2018; Yang et al., 2019). In the southern part of the Bayan Obo deposit, a granite intrusion which is in direct contact with the dolomite was dated to be emplaced around 281-262 Ma (Ling et al., 2014). Associated with this intrusion, a magnesium silicate skarn is developed, locally enriched in REE mineralization.

3 Sampling and analytical methods

3.1 Sample collection and petrography

At Bayan Obo, Mg is hosted predominantly in dolomite, with only minor amounts in silicate minerals such as aegirine and biotite. For this study, siderite carbonatites were selected for detailed investigation and compared with micritic mound dolomite, typical sedimentary carbonate rocks, and wall-rock dolomites.

Fresh siderite carbonatite samples were collected from outcrops in the Main and West Orebodies of the Bayan Obo deposit. To minimize contamination, sampling avoided weathered surfaces, hydrothermal veins, and late-stage calcite stringers. Six representative specimens were obtained at 0.5-1 m intervals. Each sample was divided into two portions: one prepared as thin sections for petrographic observation, and the other processed for geochemical and isotopic analysis. For powder preparation, weathered rinds were removed, and the fresh material was cleaned, oven-dried, and reduced to millimeter-sized chips with a jaw crusher or hand hammer. The chips were subsequently ground in an agate mortar or ball mill, sieved to 200 mesh, and reground where necessary. The resulting powders were homogenized, split into aliquots, and sealed in clean containers to ensure uniformity and minimize contamination.

The siderite carbonatite is yellow-brown in color and displays a blocky, porphyritic texture (Figure 2). Siderite phenocrysts account for \sim 90% of the primary mineral assemblage, whereas

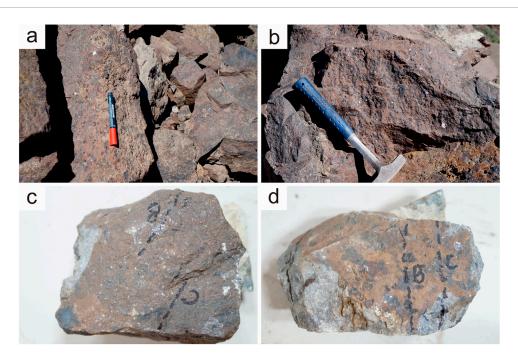


FIGURE 2
Photographs of a representative field sample (a,b) and hand specimen (c,d) of siderite carbonatites from the Bayan Obo deposit, exhibiting a porphyritic texture. The phenocrysts are predominantly composed of siderite, while the matrix consists of dolomite, magnetite, and monazite.

secondary phases include magnetite, pyrite, monazite, and calcite (Figures 3a-d). Rare earth elements are hosted mainly in monazite. The groundmass consists largely of Mg-rich siderite formed through hydrothermal alteration and metasomatism, with partial replacement by dolomite. Hydrothermal fluids enriched in Mg, Ca, Ba, F, and REE promoted decomposition of primary siderite and subsequent formation of Mg-bearing siderite, dolomite, magnetite, and monazite. Magnetite commonly occurs along fractures in carbonate minerals, accompanied by strong alteration and metasomatism. Progressive replacement of siderite results in a mineral sequence from siderite > Mg-siderite > Mg-rich siderite → dolomite → monazite ± magnetite. Back-scattered electron (BSE) imaging reveals corresponding zoning, with decreasing Fe contents expressed as a transition from bright to darker gray tones. Hydrothermal decomposition of siderite phenocrysts also generated pyrite, sericite, and quartz (Figures 3e,f), a process analogous to alteration patterns in porphyry Cu systems.

In this study, carbonatites are classified according to their dominant mineralogy as calcite, dolomite, and siderite carbonatites, consistent with widely used nomenclature in previous studies of the Bayan Obo deposit (e.g., Woolley and Kempe, 1989; Chao et al., 1997). These mineralogical terms correspond broadly to the geochemical categories of calcio-, magnesio-, and ferro-carbonatites (Le Bas, 1987), but we adopt the mineral-based terminology here because the classification of our samples is supported directly by petrographic observations and mineral compositions.

3.2 Analytical methods

3.2.1 Labware cleaning

All labware and sample containers were rigorously cleaned to prevent contamination. Specifically, we now clarify that all Teflon vials were pre-cleaned by sequential soaking in 6 N HCl and Milli-Q water, while all plastic ware was soaked in 10% HCl and thoroughly rinsed before use. All acids used were either commercially ultrapure (Optima grade) or purified further by double sub-boiling distillation.

3.2.2 Major and trace elements

Whole-rock major and trace element analyses of Bayan Obo siderite carbonatites were carried out at Yanduzhongshi Geological Analysis Laboratories Ltd., Beijing, China. Major elements were determined by X-ray fluorescence spectrometry (Zetium, PANalytical Malvern, United Kingdom) with analytical uncertainties better than 1%. Trace elements were measured by inductively coupled plasma–mass spectrometry (ICP-MS), with accuracies better than 5% relative to the GSR-2 standard. For volatile and ultra-trace elements, analytical errors did not exceed 10%.

3.2.3 Chemical purification and MC-ICP-MS analysis of Mg isotopes

All chemical procedures were conducted in a class-1000 clean laboratory under a class-100 laminar flow hood. Mineral separates or whole-rock powders (10–50 mg, depending on Mg contents) were digested in sealed Teflon beakers or high-pressure bombs

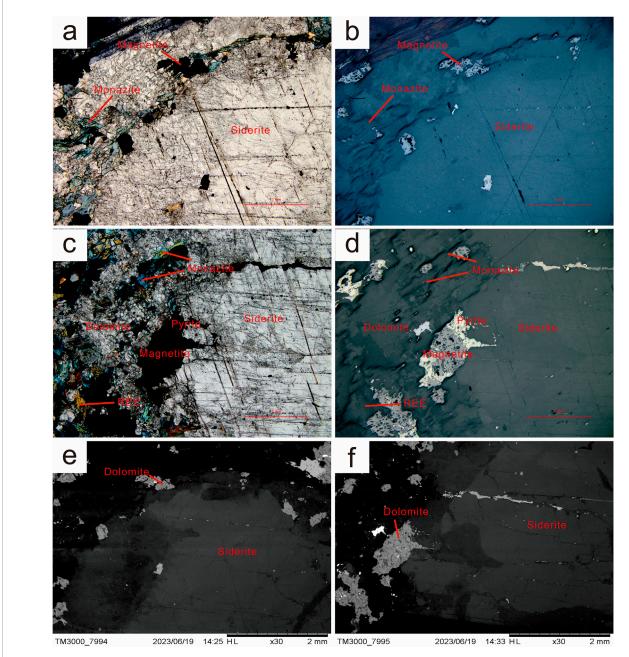


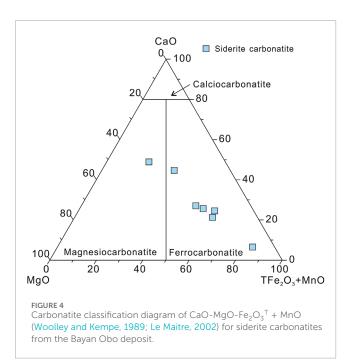
FIGURE 3
Photomicrographs in cross-polarized transmitted light (a,c), reflected light (b,d), and scanning electron microscope backscattered-electron images (e,f) of siderite carbonatites from the Bayan Obo deposit, highlighting key geological features, ore mineral assemblages, and textures within the mineralization stages. (Abbreviations: Mag, magnetite; Mnz, monazite; Sid, siderite; Dol, dolomite; Py, pyrite; Bst, bastnäsite; Whitney and Evans, 2010).

using a mixture of ultrapure HF–HNO $_3$ (3:1, v/v), prepared either from commercial ultra-pure acids or by double subboiling distillation. After initial digestion, the solutions were evaporated to dryness, treated with aqua regia, dried again, and refluxed with concentrated HNO $_3$ to eliminate residual fluorides. The final residues were dissolved in 1 N HNO $_3$ for column chromatography. No visible precipitates were present in the final solutions, and centrifugation was applied where necessary to ensure complete dissolution without measurable Mg loss.

Magnesium purification was carried out using Savillex microcolumns loaded with 2 mL of Bio-Rad AG50W-X12 (200–400 mesh) cation-exchange resin (Chang et al., 2003). Prior to use, resins were sequentially rinsed with 8 N HNO3 and Milli-Q water (18.2 M Ω) at least three times and stored in ultrapure water. Before each separation, the resins were backwashed with Milli-Q water to remove air bubbles and minimize compaction, then pre-cleaned with alternating rinses of 4 N HNO3 + 0.5 N HF and Milli-Q water, and finally conditioned with 6 mL of 2 N HNO3. Mg was purified using a two-stage cation-exchange procedure with

Data sources Sun et al. (2012) This Paper TABLE 1 The major element contents (wt.%) of siderite carbonatite, carbonatite dyke, dolomite carbonatite, sedimentary carbonate rock and microcrystalline mound dolomite from the Bayan Obo deposit. 99.93 99.97 98.88 98.03 61.8 94.6 98.3 85.3 89.2 85.6 99.3 98.7 66 91 1.03 1.03 0.53 0.37 0.58 0.01 0.01 0.12 1.82 0.24 0.04 0.89 1.82 9.36 26.72 31.61 33.37 44.28 31.0434.06 20.88 33.75 0 36.43 25.42 25.68 33.39 45.04 45.03 33.1 30.1 P_2O_5 90.0 1.24 0.45 0.26 0.37 0.58 7.6 3.99 0.54 0.44 0.38 0.61 4.75 0.04 0.01 0.01 0.2 K₂O 0.15 0.12 0.22 0.07 0.28 0.25 0.04 0.21 0.07 0.73 0.03 0.34 0.02 0.00 0.44 0.04 0.02 Na₂O 0.13 0.18 0.17 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.26 0.07 0.97 0.25 0.02 0.04 0.05 CaO 14.63 29.69 23.96 29.75 26.58 21.64 29.75 29.74 25.77 16.24 4.54 16.61 16.4 15.61 22.3 30.3 MgO 14.49 17.86 11.22 12.86 20.64 18.64 12.02 14.94 20.78 9.9 8.82 8.45 10.9 5.08 MnO 4.94 2.83 1.03 3.82 3.76 0.36 1.46 99.0 2.86 1.69 2.38 96.0 0.09 0.08 0.07 TFe_2O_3 53.35 30.44 15.11 8.83 27.08 35.32 36.93 1.59 3.58 8.56 13.72 26.25 96.0 0.63 8.24 0.59 7.4 Al_2O_3 0.15 0.16 0.92 0.95 69.0 0.79 0.14 0.05 0.08 0.07 0.71 0.94 0.87 0.98 90.0 1.33 0.04 0.37 0.07 0.01 0.08 0.09 0.02 0.12 0.01 0.130.18 0.05 0.07 0.01 0.21 0.01 0 26.07 2.18 1.91 3.01 2.02 3.7 0.55 2.04 1.61 0.71 1.93 0.22 1.77 2.76 3.1 7.7 Samples BY21801D BY23207B BY23005D BH-09-17 BN-09-13 BN-09-35 BN-09-44 BE-09-22 BN-09-68 BH-09-14 BE-09-30 BE-09-16 BN-09-64 BY23116 B5334-1 B2133D B5335-2 Microcrystalline mound dolomite Sedimentary carbonate rock Sample types Dolomite carbonatite Siderite carbonatite Carbonatite dyke

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AG50W-X12 resin. In the first stage, Mg and Na were separated from other cations on a long resin column by elution with 2 N HCl. In the second stage, Na was removed from Mg on a short resin column by sequential elution with 0.4 N HCl (to wash away Na) and 6 N HCl (to elute Mg). The purified Mg fractions were collected, evaporated to dryness, and converted into an HNO₃ medium. Prior to MC-ICP-MS analysis, the solutions were diluted to appropriate concentrations in 0.1 N HNO₃. The overall Mg recovery through the purification procedure was >99.99%.

Magnesium isotope ratios were measured using a Nu Plasma high-resolution multicollector ICP-MS (MC-ICP-MS). Samples introduced through a DSN-100 desolvation nebulizer were mixed with 0.3 mol/L HNO3 prior to analysis. Sample and standard solutions were matched in concentration (~1 $\mu g/ml$ Mg), with differences maintained within 10%. Background signals were measured before each analytical block, and data were acquired as sets of ten ratios with 10 s integration times. Instrumental mass bias was corrected by sample–standard bracketing, a procedure that minimizes matrix effects and ensures accurate and reproducible Mg isotope results. The instrument control system is comparable to that of the Nu Plasma HR-MC-ICP-MS at Oxford University (Belshaw et al., 2000). Magnesium isotope compositions are reported in standard δ notation as:

$$\delta^i Mg = \left[\left({}^i MG/^{24} MG \right)_{sample} / \left({}^i MG/^{24} MG \right)_{DSM3} - 1 \right] \times 1000, i = 25 \text{ or } 26,$$

relative to the DSM3 standard, with uncertainties reported at the per mil (‰) level.

3.2.4 Data quality

To ensure the reliability of concentration and Mg isotope compositions, procedural blanks were routinely measured and used to correct all sample measurements. Both concentration and isotopic data were corrected for blank contributions. The total blank was

 $<\!10$ ng for Mg, which is negligible compared to the sample Mg mass (typically 1–5 μg). The isotopic composition of the blanks was indistinguishable from the bracketing standard within analytical uncertainty. Both concentration and isotopic data were corrected for blank contributions using:

$$R_{\text{corrected}} = (R_{\text{measured}} \times M_{\text{sample}} - R_{\text{blank}} \times M_{\text{blank}}) / (M_{\text{sample}} - M_{\text{blank}}),$$

where R represents the isotopic ratio and M denotes the Mg mass of the sample or blank. The propagated uncertainties include analytical repeatability, blank corrections, and instrumental uncertainties. Long-term bracketing standards analyzed on the MC-ICP-MS demonstrated reproducibility better than $\pm 0.07\%$ (2SD) in δ^{26} Mg over the analytical period. Procedural standards processed alongside samples confirmed >99% Mg recovery with no detectable isotope fractionation. The combined uncertainties are reported for all concentration and isotopic measurements.

4 Analysis results

4.1 Major element oxides

The major element compositions of the samples are shown in Table 1. Siderite carbonatites are dominated by TFe₂O₃, MgO, CaO, and MnO, with TFe₂O₃ content between 8.83% and 53.35%, MgO content between 6.60% and 17.86%, CaO content between 4.54% and 26.58%, and MnO content between 1.03% and 4.94%, while SiO₂, Al₂O₃, Na₂O, K₂O, TiO₂ and P₂O₅ content are low. Compared with global average carbonatites, Bayan Obo siderite carbonatites are notably Mg-enriched and Ca-deficient. Their chemical composition is broadly similar to dolomitic carbonatites and wall-rock dolomites, but differs significantly from sedimentary dolomites and micritic mound dolomites in the deposit. Previous studies classified carbonatites as calcareous, magnesian, or ferritic carbonatites based on CaO, MgO, and TFe₂O₃+MnO contents (Woolley and Kempe, 1989). As shown in Figure 4, Bayan Obo siderite carbonatites predominantly fall into the ferro (iron-rich) carbonatite category.

4.2 Trace and rare earth elements

The trace and rare earth element compositions of the Bayan Obo siderite carbonatites differ markedly from those of sedimentary carbonate rocks and are broadly comparable with dolomite carbonatites (Table 2). The total REE (Σ REE) ranges from 2,696.75 to 20,763.57 ppm. The REE patterns are right-skewed, indicating pronounced light rare earth elements (LREE) enrichment (La/Yb_N = 129.15–1,681.51) and heavy rare earth elements (HREE) depletion. Ce shows slight positive anomalies, while Eu exhibits moderate negative anomalies, suggesting variable oxidation states during mineral formation (Figure 5b). Trace elements such as Ba, Th, and Nb show significant positive anomalies, likely reflecting contributions from accessory minerals (e.g., monazite, bastnäsite), whereas Rb, U, Ta, and Zr display strong negative anomalies (Figure 5a). Compared with sedimentary carbonate rocks, the siderite carbonatites are notably enriched in Mg, Fe, and LREE, consistent

14,038.57

王

120.

LREE

9,967.02

4,361.1

9,441.

278.45

0.65

2.82

2,518.053

2,629.85

961.63

168.84

11,593.01

1765.6

0.36

129.15

53.33

247.45

173.87

7,161.

1.25

1,604.

26.83

0.2

2.61

1,147.

6,343.1

0.05

123.65

1,205.94

8.87

0.61

960.02

40.01

65.76

252.

1.83

810.9

1.23

7.62

866.579

667.12

0.03

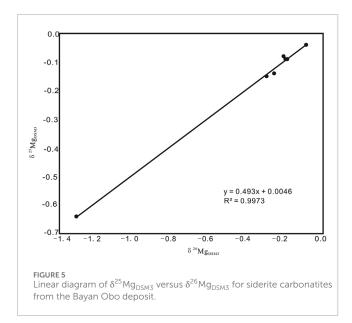
495.38

25.14

137.35

14,301.81 10,244.27 4,450.83 7,940.69 2,696.75 9,671 1.35 12.02 7.11 124.12 15.44 64.73 38.65 .472 5,424.074 266.953 1941 그 0.41 0.3 0.21 0.11 0.2 3,236.05 4,723.83 2,333.44 PΖ 1.63 1.22 ð 4.03 1.9 1.01 ᆵ 852.12 0.75 0.37 0.22 0.47 0.54 0.11 0.29 796.3 27.19 14.81 4.51 4.98 0.11 2.22 운 1.06 0.83 2.38 1.99 2.31 3,370.34 229.05 96.966 9 N 38.17 14.49 7.86 8.05 5 0.85 0.5 16.13 13.46 11.4 29.2 4.93 12.3 TABLE $2\,$ Analysis results of rare earth and trace elements (10- 6) in siderite carbonatite from the Bayan Obo deposit. 4.1 184.23 78.17 234.1 375.46 217.34 70.18 196.5 9 182.1 117.78 84.76 29.16 38.46 32.36 59.98 30.84 Ga 20.13 2,301 1783. 12.76 8.48 E 128.15 157.37 174.88 5.61 9.91 340.61 133.54 59.1 8Ce 1.01 6.0 3,236.05 4,723.83 2,333.44 743.66 PZ 667. 0.33 1,340.81 704.79 265.17 195.19 857.23 866.89 (La/Yb) 297.88 736.68 1,928.65 1,102.89 4,548.17 4,298.62 6,582.51 Ce LREE/HRI 1,351.76 3,821.09 1951.33 607.43 426.71 La BY21801D BY23207B BY23116 BY23005D B2133D B5335-2 HREE 277.25 480.46 229.27

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with their magmatic-hydrothermal origin. The geochemical characteristics provide insights into the fractionation processes and metallogenic environment of the deposit.

4.3 Mg isotopes

Test data correctness is often checked by comparing numerical values to established reference materials. For Mg isotopes, however, no internationally recognized standard currently exists due to limited data. All $\delta^{26} Mg$ and $\delta^{25} Mg$ values in this study fall along the mass-dependent fractionation line (Figure 6), indicating negligible isobaric interferences during MC-ICP-MS analysis. Mg isotope results for the samples are listed in Table 3, with δ^{26} Mg ranging from -1.31 to -0.09‰ and δ^{25} Mg from -0.64 to -0.08‰. Figure 7 places these results in context, comparing them with previously reported ranges for carbonate wall rocks $(\delta^{26}\text{Mg} = -1.67 - 1.50\%)$, dolomites (-2.31 - -1.05%), dolomite carbonatites (-1.12--0.31%), sedimentary carbonate rocks (-1.53--1.51%), and mantle rocks (-0.52-0.23%) (Galy et al., 2002; Chang et al., 2003; Tipper et al., 2006b; Wiechert and Halliday, 2007; Handler et al., 2009; Bourdon et al., 2010; Teng et al., 2010a; Yang et al., 2012; Sun et al., 2012; Sun, 2013).

5 Discussion

5.1 Features of the siderite carbonatite source area

The origin of carbonatites has been a subject of debate, reflecting the complexity of the source region's composition. Some scholars suggest that certain carbonatites may not directly originate from mantle-derived melts, but instead form through a contact metasomatic process within a permeable magmahydrothermal system (Lentz, 1999). However, the mainstream

view generally holds that carbonatites primarily result from lowdegree partial melting of the mantle, and differentiation processes such as fractional crystallization or hydrous melt immiscibility (Le Maitre, 2002; Jones et al., 2013; Lentz, 2014; Vladykin and Pirajno, 2021). The siderite carbonatites in this study have similar geochemical characteristics to the dolomite carbonatites (Figure 7), suggesting that they may have originated from the same magma source. Dolomite carbonatites have an $\varepsilon_{Nd}(t)$ value ranging from -2.72 to -0.51, and a low (87 Sr/ 86 Sr)_i value (0.70341-0.70590) (Zhang Z. Q. et al., 2001), indicating little contamination from lower crust minerals (Simonetti et al., 1995; Hou et al., 2006). Research suggests that the genesis of carbonatites with εNd<0 may be related to the mixing of High U/Pb mantle unit - Enriched mantle I (HIMU-EM I) endmembers (Simonetti et al., 1995; Tilton et al., 1998). Therefore, the source area of the Bayan Obo siderite carbonatites may be a complicated mantle source generated by the mixing of HIMU and EM II mantle end components.

Fluid metasomatism in subducting marine sediments is thought to be the cause of rare earth enrichment in mantle source area associated with carbonate rocks (Hou et al., 2015). The Bayan Obo siderite carbonatites exhibit high Sr (796.3-6,343.1 ppm), Ba (84.8-11,593.0 ppm), and LREE (2,631.0-20,283.1 ppm) (Figure 8), as well as a high Ba/Th ratio (0.64-68.66) characteristics, which supports the fluid metasomatism model in sediments. Diving marine sediments are rich in REE and CO2 fluids, which typically have high concentrations of large ion lithophile elements (LILE) and relatively low quantities of high field strength elements (HFSE), resulting in high LILE/HFSE ratios (Turner et al., 1997; Elburg et al., 2022). This type of CO₂ rich fluid metasomatism produces carbonate rocks enriched in LILE and REE. During partial melting, HFSE, HREE, and others are retained in the titanium iron oxide, whereas LILE and LREE preferentially penetrate the melt (Foley et al., 2000; Gaetani et al., 2008; Hammouda et al., 2009). This explains the reason for the enrichment of rare earth elements in the mantle source region.

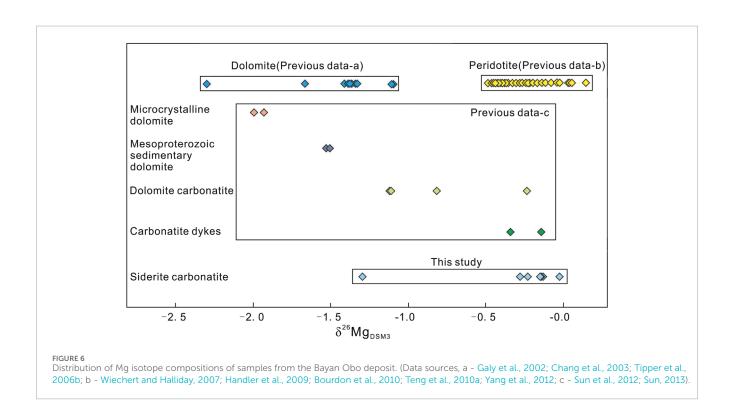
5.2 Mg isotope system in nature

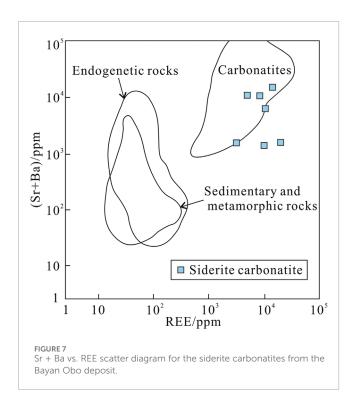
Magnesium is a primary rock-forming element widely distributed in the mantle, crust, and hydrosphere. In the mantle and crust, Mg mainly occurs in silicate minerals such as olivine, pyroxene, and mica, as well as in carbonates such as dolomite. In the hydrosphere, Mg is the most abundant metallic element in both river water and seawater. Previous studies have documented systematic isotopic differences among these reservoirs (Figure 9).

The upper mantle exhibits a relatively homogeneous Mg isotopic composition. Chondrites, mantle peridotites, and basalts yield δ^{26} Mg values of -0.49 to +0.06%, averaging around -0.24% (Ke et al., 2011), indicating a narrow mantle range. In contrast, the continental crust, especially the upper crust, shows significant isotopic heterogeneity. Soils are commonly enriched in heavy Mg isotopes relative to basalt, whereas sedimentary carbonates are generally isotopically lighter. Carbonates display large variations (δ^{26} Mg = -4.84 to -1.00%; Galy et al., 2002; Tipper et al., 2006a; Tipper et al., 2006b; Pogge von Strandmann et al., 2008). Within this group, dolomite tends to have relatively heavier values (-2.29 to -1.09%), whereas limestones are

TABLE 3 Mg isotopic compositions of siderite carbonatite, carbonatite dyke, dolomite carbonatite, sedimentary carbonate rock and microcrystalline mound dolomite from the Bayan Obo deposit.

Sample types	Samples	δ ^{26/24} MgDSM3‰	2SD	$\delta^{25/24}$ MgDSM3‰	2SD	n	Data sources
Siderite carbonatite	BY23207B	-0.26	0.05	-0.14	0.04	3	This Paper
	B2133D	-1.31	0.05	-0.64	0.04	3	
	BY21801D	-0.19	0.01	-0.09	0.02	3	
	BY23116	-0.09	0.05	-0.04	0.03	3	
	BY23005D	-0.2	0.04	-0.09	0.03	3	
	B5334-1	-0.21	0.03	-0.08	0.02	3	
	B5335-2	-0.3	0.02	-0.15	0.01	3	
Carbonatite dyke	BN-09-13	-0.14	0.18	-0.05	0.08	4	Sun et al. (2012)
	BN-09-35	-0.34	0.11	-0.16	0.05	7	
Dolomite carbonatite	BN-09-44	-0.81	0.06	-0.2	0.03	12	
	BE-09-16	-1.12	0.2	-0.56	0.11	2	
	BE-09-22	-0.31	0.09	-0.14	0.04	10	
	BE-09-30	-1.11	0.09	-0.55	0.06	4	
Sedimentary carbonate rock	BN-09-64	-1.5	0.11	-0.76	0.08	5	
	BN-09-68	-1.67	0.03	-0.85	0	2	
Microcrystalline mound dolomite	BH-09-14	-1.99	0.04	-1.01	0	2	
	BH-09-17	-1.93	0.13	-0.96	0.05	2	





lighter (-4.47 to -2.43%). Such differences reflect equilibrium fractionation among dolomite, calcite, and water (Galy et al., 2002). Stalactites and foraminifera yield even lighter δ^{26} Mg values, indicating significant biological or low-temperature fractionation (Chang et al., 2004; Pogge von Strandmann et al., 2008).

In the hydrosphere, seawater is isotopically uniform ($\delta^{26} \text{Mg} \approx -0.83\%$; Chang et al., 2003; Young and Galy, 2004; Ling et al., 2011), consistent with its long residence time (>10 Ma; Li, 1982). By contrast, continental waters are highly variable: river waters range from -2.08 to -0.52% (Young and Galy, 2004; Tipper et al., 2006a; Tipper et al., 2006b; Brenot et al., 2008).

The mechanisms controlling these variations are well established. High-temperature magmatic processes produce only minor Mg isotope fractionation (Teng et al., 2007; Teng et al., 2010a; Liu et al., 2010), whereas low-temperature water-rock interaction induces large isotopic shifts (Galy et al., 2002; Chang et al., 2004; Young and Galy, 2004; Pogge von Strandmann et al., 2008). Weathering of silicate rocks preferentially removes light Mg isotopes into solution, leaving soils isotopically heavy and rivers/seawater relatively light (Tipper et al., 2006a; Tipper et al., 2006b; Brenot et al., 2008). During carbonate precipitation, sediments preferentially incorporate light isotopes (Galy et al., 2002; Chang et al., 2004).

Against this global framework, our new data show that the Bayan Obo siderite and dolomite carbonatites have distinctly heavier $\delta^{26} Mg$ values than Mesoproterozoic sedimentary dolomites from the same region (Figure 9). This isotopic distinction demonstrates that the Bayan Obo ore-bearing carbonatites cannot be explained by a simple sedimentary origin, and instead show closer affinity to mantle values with only limited modification from wall-rock interaction. These results provide a critical baseline for constraining the genetic models of the deposit.

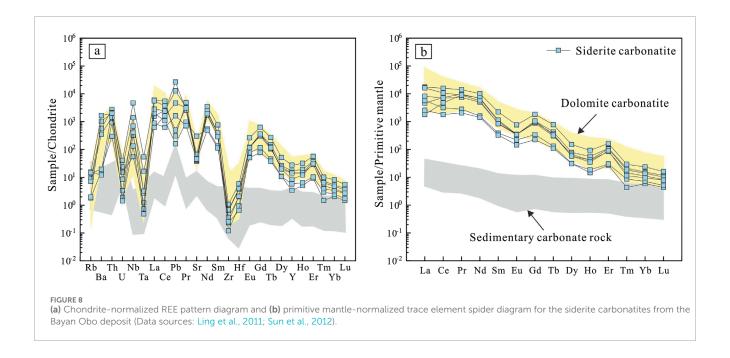
5.3 Constraints on genesis of the Bayan Obo deposit

The genesis of the Bayan Obo ore-bearing dolomite carbonatites has been widely debated, with models including: (1) microbial or diagenetic micritic mounds genesis, which emphasizes microbial or early diagenetic processes (Qiao et al., 1997; Zhang P. S. et al., 1998); (2) normal sedimentary genesis, proposing a typical marine carbonate sedimentation origin (Meng, 1982; Meng and Drew, 1992; Wei and Shangguan, 1983); and (3) primary carbonatite genesis, which interprets the dolomite carbonatites as direct products of mantle-derived carbonatitic magmatism (Bai et al., 1996; Le Bas et al., 1997; Mitchell, 2005; Yang and Le Bas, 2004). Mineralogical and geochemical features suggest classification of the Bayan Obo siderite carbonatites as magmatic carbonatites (Mitchell, 2005), and the Mg isotope data presented here provide new constraints on these interpretations.

5.3.1 Possibility of the formation of micrite mound

Micrite mound, also known as carbonate mud mound, is mainly composed of plaster, with only a small number of organisms and biological debris (Fan and Zhang, 1985). Macroscopically, it is generally a discus-shaped body having a convex top and a flat bottom, with the thickness ranging from a few meters to many tens of meters. It appears in a strip parallel to the ancient coastline in areas with deeper water slopes (Qiao et al., 1997). Typical micrite mound in China include: the top micrite mound of the Cambrian system in Xishan, Beijing, and the top micrite mound of the Sailinhudong Group in the Heinaobao area of Inner Mongolia (about 25 km southeast of the Bayan Obo mining area) (Qiao et al., 1997). Qiao et al. (1997) compared the ore-bearing dolomite carbonatite of the Bayan Obo deposit with the micrite mound of the Sailinhudong area, and suggested that the two may belong to the same stratigraphic horizon based on their macroscopic geological features. Subsequently, Zhang Y. X. et al. (1998), Zhang et al. (2008) argued that the micritic carbonates in the Bayan Obo deposit formed as products of seafloor hydrothermal activity (with CO₂ involvement), primarily by chemical sedimentation, with REE, Nb, Na, and F sourced from deep hydrothermal fluids, and Ca, Mg, and Fe mainly derived from seawater.

Our Mg isotope results provide new geochemical constraints on this issue. The Bayan Obo siderite carbonatites (δ^{26} Mg = -1.31--0.09%) and dolomite carbonatites (δ^{26} Mg = -1.12--0.31%) display significantly higher values than Mesoproterozoic sedimentary dolomites (δ^{26} Mg = -2.50--2.00%), but are distinguishable from the Sailinhudong micrite mound dolomites (δ^{26} Mg = -1.99--1.93%) (Figure 9). These observations indicate that, although the Mg isotopic composition of Bayan Obo carbonatites partly overlaps with sedimentary fields, they are clearly shifted relative to the Sailinhudong micrite mound dolomites. This offset suggests that the Bayan Obo carbonatites cannot be simply interpreted as equivalents of the Sailinhudong micrite mounds, and therefore Mg isotopes highlight the difficulty of establishing a direct genetic relationship between the two.



5.3.2 Possibility of normal sedimentary genesis

Previous study indicates that the Mg isotope composition of sedimentary dolomites varies significantly (δ^{26} Mg is -2.29--1.09%; Galy et al., 2002; Chang et al., 2004; Tipper et al., 2006b; Brenot et al., 2008). This might be related to factors like varying ages or geological backgrounds of dolomite. To compare with the dolomite carbonatites from the Bayan Obo deposit, it is necessary to obtain the Mg isotope composition of the sedimentary dolomites in the H8 rock section of the Bayan Obo Group. This can be obtained from the Kuangou north sedimentary dolomite, whose δ^{26} Mg is -1.67 --1.54%. This should represent the Mg isotope composition characteristics of the dolomites in the H8 rock section of the Bayan Obo Group. Moreover, the δ^{26} Mg of the Middle Proterozoic dolomite in Pingquan area is -1.81--1.53‰, consistent with the Mg isotope of the sedimentary dolomites in Kuangou north. This suggests that the sedimentary dolomites in Bayan Obo Pingquan area during the Middle Proterozoic period has a consistent Mg isotope composition. The δ^{26} Mg of sedimentary dolomites from the Middle Proterozoic in the Bayan Obo area should be -1.81 - -1.53%.

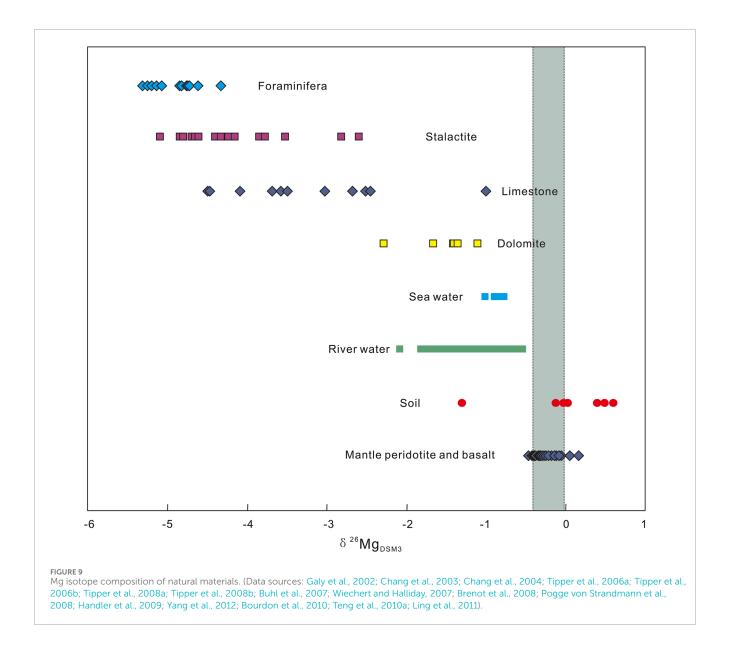
The δ^{26} Mg isotope compositions of the dolomite carbonatites and extracted siderite carbonatite samples from Bayan Obo are significantly heavier than those of Mesoproterozoic sedimentary dolomites, with none of the samples falling within the δ^{26} Mg range of the sedimentary dolomites (Figure 9). This suggests that the ore-bearing dolomite carbonatites are not normally deposited dolomites. The elevated δ^{26} Mg values may result from magmatic differentiation and hydrothermal processes, which preferentially retain heavy Mg isotopes in the residual carbonatites. In addition, fluid–rock interaction, partial recrystallization, or carbonate precipitation from Mg-rich deep fluids could further modify the Mg isotope composition, distinguishing these carbonatites from sedimentary dolomites formed under surface depositional conditions.

5.3.3 Possibility of magmatic genesis

The Mg isotopic ratios of the carbonatites exhibit a broader range than those of the Mesoproterozoic sedimentary dolomites (Figure 6). This variability likely reflects the superposition of several processes: (1) magmatic differentiation and fractional crystallization, which generate isotopic heterogeneity in the carbonatite system; (2) hydrothermal alteration and fluid–rock interaction, which preferentially mobilize light Mg isotopes and shift isotopic compositions; and (3) post-depositional recrystallization of carbonates, which may further modify primary signatures. Together, these processes account for the wider spread of δ^{26} Mg values in the carbonatites compared with the relatively homogeneous dolomites.

Magnesium isotope fractionation is strongly temperature dependent. At magmatic temperatures, equilibrium fractionation is generally limited (Pogge von Strandmann et al., 2011; Ling et al., 2011), whereas at low temperatures water-rock interaction can produce significant fractionation (Galy et al., 2002; Chang et al., 2004; Young and Galy, 2004; Pogge von Strandmann et al., 2008; Teng et al., 2010a; Teng et al., 2010b). During silicate magmatic differentiation, light Mg isotopes partition preferentially into fluids, enriching residual silicates in heavy isotopes, whereas rivers and seawater are relatively enriched in light isotopes (Tipper et al., 2006a; Tipper et al., 2006b; Tipper et al., 2008a; Tipper et al., 2008b; Brenot et al., 2008). In contrast, carbonate precipitation favors incorporation of light isotopes into the solid phase (Galy et al., 2002; Chang et al., 2004).

In the Bayan Obo siderite carbonatites, some samples yield exceptionally light δ^{26} Mg values (-1.31‰), far lower than mantle compositions. Possible causes include magmatic differentiation, weathering, hydrothermal alteration, wall-rock assimilation, and fluid exsolution during magma ascent (Teng et al., 2011; Chen et al., 2020). Experimental studies show that silicate–carbonate isotope exchange at high temperatures favors retention of heavy Mg isotopes in silicate melts, leaving carbonates isotopically lighter (Schauble, 2011; Macris et al., 2013). Liquid immiscibility and fractional



crystallization of carbonatite melts may further produce $\sim 0.2\%$ fractionation (Li et al., 2016), though this alone cannot account for the extremely light δ^{26} Mg values observed.

Crustal contamination is unlikely to be the sole explanation, as crustal rocks generally overlap mantle values (-0.40-+0.12%; Rudnick and Gao, 2014; Huang et al., 2013; Cheng et al., 2017). Instead, assimilation of Mg-rich carbonate wall rocks is more consistent with the data. Local dolostones exhibit lighter δ^{26} Mg values (-1.81--1.53%), and petrographic evidence reveals marble xenoliths within the carbonatites. Thus, wall-rock assimilation, likely enhanced by fluid exsolution during magma ascent, offers a plausible mechanism for the isotopically light signatures in Bayan Obo siderite carbonatites.

Overall, the Mg source of the Bayan Obo carbonatites is dominantly mantle-derived, but the observed isotopic heterogeneity reflects overprinting by fractional crystallization, liquid immiscibility, hydrothermal alteration, and particularly wall-rock assimilation.

Independent isotopic systems corroborate this interpretation. (1) S isotopes: Sulfides (pyrite, galena) display mantle-like sulfur isotope compositions, whereas whole rocks and barites fall between mantle and seafloor sedimentary sulfate endmembers (Ding et al., 2003). (2) Sr–Nd isotopes: The deposit shows clear mantle signatures (Zhang et al., 2003). (3) C–O isotopes: $\delta^{13}C_{V-PDB}$ and $\delta^{18}O_{V-SMOW}$ values of siderite carbonatites (-3.66--0.13% and 10.89-13.66%, respectively) resemble dolomite carbonatites and fall within the range between primary igneous carbonatites and sedimentary rocks (Liu, 1986; Cao et al., 1994; Wei et al., 2022). In contrast, sedimentary dolostones and other carbonates typically yield $\delta^{13}C > -4\%$ and $\delta^{18}O > 18\%$ (Tang, 2022). These combined data indicate that Bayan Obo mineralization was driven by mantle-derived carbonatitic magmatism with localized carbonate assimilation during magma degassing.

An alternative model proposes that sedimentary carbonate rocks were directly replaced by mantle-derived carbonatites or fluids. This scenario is inconsistent with current observations. First, the majority

of siderite carbonatite δ^{26} Mg values fall within the mantle range, with no samples overlapping sedimentary endmembers, indicating a dominant mantle Mg source. Second, if sedimentary carbonate rocks had been extensively replaced, isotopic compositions would more strongly retain sedimentary characteristics at lower δ^{26} Mg values, reflecting incomplete metasomatism. Instead, Bayan Obo siderite carbonatites are characterized by low SiO_2 and CaO, but high TFe_2O_3 , MgO, MnO, and REE (Table 1), with pronounced enrichment in LREE and incompatible elements such as Sr and Ba. These geochemical traits match mantle-derived igneous carbonatites and sharply contrast with sedimentary carbonates, which typically contain <200 ppm Sr + Ba and <25 ppm REE (Kang et al., 2024).

Taken together, isotopic and geochemical evidence demonstrates that the Bayan Obo siderite carbonatites are best explained as products of mantle-derived carbonatitic magmatism that experienced substantial modification by fractional crystallization, immiscibility, hydrothermal alteration, and wallrock assimilation, rather than by wholesale replacement of sedimentary carbonate rocks.

6 Conclusion

- 1. The Bayan Obo siderite carbonatites are characterized by high concentrations of TFe₂O₃, MgO, and MnO, and low contents of SiO₂, K₂O, Na₂O, and P₂O₅—geochemical features typical of ferro carbonatites. In terms of trace element composition, these rocks are enriched in Ba, Sr, Th, and REE, exhibiting geochemical signatures similar to those of the orebearing dolomite carbonatites, but distinct from sedimentary carbonate rocks. When integrated with previous studies, these characteristics support the interpretation that the Bayan Obo siderite carbonatites may have originated from a mantle source influenced by mixing between HIMU and EM I components.
- 2. The δ^{26} Mg values of the Bayan Obo siderite carbonatites range from -1.31 to -0.09%, clustering near the mantle endmember. Their Mg isotope compositions closely resemble those of the ore-bearing dolomite carbonatites, supporting a mantle-derived magmatic origin for both rock types.
- 3. Combining the results of this study with previous research, we propose that the Bayan Obo deposit formed through carbonatitic magma intrusion and associated metasomatism. The genesis of the deposit was primarily controlled by mantle-derived carbonatitic magmatism, with subsequent magma differentiation and evolution likely driving the enrichment of Fe, REE, Sr, Ba, and Y.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

CR: Writing – original draft, Conceptualization, Methodology. HJ: Writing – review and editing, Supervision. QZ: Writing – review and editing. HS: Writing – review and editing, Supervision, Formal analysis, Funding acquisition. JL: Writing – review and editing. BL: Writing – review and editing.

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Conflict of interest

Author QZ was employed by PetroChina Xinjiang Oilfield Company.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The reviewer WJ declared a shared affiliation with the authors CR, HJ, HS, JL, BL to the handling editor at time of review.

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